

# Effect of local Coulomb interactions on the electronic structure and exchange interactions in $Mn_{12}$ magnetic molecules

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We have studied the effect of local Coulomb interactions on the electronic structure of the molecular magnet  $Mn_{12}$ -acetate within the LDA+U approach. The account of the on-site repulsion results in a finite energy gap and an integer value of the molecule's magnetic moment, both quantities being in a good agreement with the experimental results. The resulting magnetic moments and charge states of non-equivalent manganese ions agree very well with experiments. The calculated values of the intramolecular exchange parameters depend on the molecule's spin configuration, differing by 25–30% between the ferrimagnetic ground state and the completely ferromagnetic configurations. The values of the ground-state exchange coupling parameters are in reasonable agreement with the recent data on the magnetization jumps in megagauss magnetic fields. Simple estimates show that the obtained exchange parameters can be applied, at least qualitatively, to the description of the spin excitations in  $Mn_{12}$ -acetate.

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## Introduction

Single-molecule magnets represent a new class of “zero-dimensional” magnetic materials consisting of almost non-interacting, identical point-like nanoscale entities<sup>1,2,3</sup>. These magnetic molecules have attracted a great deal of attention from physicists as well as chemists for detailed studies of many novel aspects of mesoscale magnetism, such as quantum spin tunneling, spin relaxation of mesoscopic magnets, the implications of the topological spin phase (Berry phase), etc.<sup>4,5,6,7,8,9,10</sup>. The  $Mn_{12}O_{12}[\text{CH}_3\text{COO}]_{16}\cdot 4\text{H}_2\text{O}$  compound<sup>11,12</sup>, often referred to as  $Mn_{12}$ -acetate or simply  $Mn_{12}$ , is one of the best-studied examples of this kind of materials. Relatively slow dynamical processes taking place in not too strong magnetic fields, when the intramolecular spin excitations can be ignored, have been widely studied in experiments, and the properties of the ground-state multiplet  $S = 10$  are known very well. Correspondingly, most of the theoretical treatments of  $Mn_{12}$  have been based on the rigid-spin model (see e.g. Refs. 13,14,15, 16,17,18,19,20,21,22), assuming that the molecule's magnetic subsystem can be represented as a single collective spin  $S = 10$ . On the other hand, the internal magnetic and electronic structure of the  $Mn_{12}$  molecules and the intramolecular interactions responsible for the formation of the molecule's collective spin have been studied in less detail. Several experiments including inelastic neutron scattering<sup>23</sup>, megagauss field magnetization measurements<sup>24</sup>, and optical absorption<sup>25</sup> have been performed to clarify the internal properties of the  $Mn_{12}$  molecules. The experimental data have been analyzed within the spin-Hamiltonian approach<sup>24,26</sup>, however, the resulting information was not systematic, and often did not lead to unequivocal conclusions (see e.g. the discus-

sion of different parameter sets in Ref. 26).

Another approach to investigate intramolecular properties is *ab initio* electronic structure calculations. So far, density-functional computations of the electronic structure for  $Mn_{12}$  have been carried out within the local density approximation (LDA)<sup>27</sup> and generalized gradient approximation (GGA)<sup>28,29</sup>. It is well known that for transition metal-oxide systems the standard density functional methods (LDA or GGA) do not give reliable information on the energy gaps and magnetic superexchange interactions<sup>31,32,33,34,35</sup>, and many-body effects should be taken into account at least in the simplest form of the LDA+U approximation<sup>36</sup>. This is essential, e.g., for an adequate description of the electronic structure and the spin excitation spectra in  $MnO$ <sup>37,38</sup>.  $Mn_{12}$ -acetate is also an insulating metal-oxide system with an energy gap of order<sup>25</sup> of 2 eV, whereas the existing calculations<sup>27,28,29</sup> give a finite density of states (DOS) and small pseudogap at the Fermi level. As a result, the total spin per molecule turns out to be non-integer, in contradiction with experimental results. Furthermore, the intramolecular exchange couplings in  $Mn_{12}$  have never been calculated before. The GGA calculations have recently been performed<sup>30</sup> for another single-molecule magnet,  $V_{15}$ , but the resulting values had to be reduced by a factor of three to achieve an agreement with the experiments. This difference could also be caused by the neglect of the on-site Coulomb repulsion, since the latter is known to decrease the calculated exchange interactions in the metal-oxide compounds<sup>37,38</sup>.

In this work, we present the results of first-principle LDA+U calculations of the electronic structure and exchange interactions for  $Mn_{12}$ . We show that the account of the many-body effects within the LDA+U approximation gives a reasonable picture of the electronic structure,

with a finite energy gap and an integer value of the total spin of the molecule. Moreover, for the first time we present the calculated data for the intramolecular exchange constants in  $\text{Mn}_{12}$ . We discuss the results of our calculations and compare them with the existing experimental data and previous theoretical studies.

The rest of the paper is organized as follows. In Section I we describe the computational scheme and the approximations employed in this work. In Section II the resulting electronic structure and calculated magnetic moments in  $\text{Mn}_{12}$  are presented. Section III is devoted to the computation of the intramolecular exchange interactions. The conclusions are presented in Section IV.

## I. SCHEME OF CALCULATIONS

The calculations have been performed for the crystal structure found by T. Lis<sup>11</sup> with the simplifications similar to those made in Ref. 29 (all the methyl groups  $\text{CH}_3$  have been replaced by hydrogen atoms and the water molecules were omitted). Therefore, the real calculations have been done for the system  $\text{Mn}_{12}\text{O}_{12}(\text{HCOO})_{16}$ . Part of this system is sketched in Fig. 1, showing the arrangement of the manganese ions and the oxygens bridging them.

To start the LDA+U calculations one needs to identify the regions where the atomic characteristics of the electronic states have largely survived (“atomic spheres”). Within these atomic spheres one can expand an electron wave function in terms of a localized orthonormal basis  $|inlm\sigma\rangle$  ( $i$  denotes the site,  $n$  is the main quantum number,  $l$  — orbital quantum number,  $m$  — magnetic number and  $\sigma$  — spin index). The density matrix is defined as

$$n_{mm'}^\sigma = -\frac{1}{\pi} \int^{E_F} \text{Im} G_{inlm, inlm'}^\sigma(E) dE, \quad (1)$$

where  $G_{inlm, inlm'}^\sigma(E) = \langle inlm\sigma | (E - \hat{H})^{-1} | inlm'\sigma \rangle$  are the elements of the Green function matrix in this localized representation (the effective Hamiltonian  $\hat{H}$  will be defined later). In terms of the elements of this density matrix  $\{n^\sigma\}$ , the generalized LDA+U functional<sup>36</sup> has the following form

$$E^{\text{LDA+U}}[\rho^\sigma(\mathbf{r}), \{n^\sigma\}] = E^{\text{LSDA}}[\rho^\sigma(\mathbf{r})] + E^U[\{n^\sigma\}] - E_{dc}[\{n^\sigma\}] \quad (2)$$

Here  $\rho^\sigma(\mathbf{r})$  is the charge density for the electrons with the spin  $\sigma$ , and  $E^{\text{LSDA}}[\rho^\sigma(\mathbf{r})]$  is the standard LSDA functional. Eq. (2) asserts that the LSDA suffices in the absence of orbital polarizations, which are given by

$$E^U[\{n\}] = \frac{1}{2} \sum_{\{m\}, \sigma} \langle m, m'' | V_{ee} | m', m''' \rangle n_{mm'}^\sigma n_{m''m'''}^{-\sigma} + (\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m''', m' \rangle) n_{mm'}^\sigma n_{m''m'''}^\sigma, \quad (3)$$

where  $V_{ee}$  is the screened electron-electron interactions. The matrix elements of  $V_{ee}$  are defined via an average Coulomb parameter  $U$  and the Hund intra-atomic exchange constant<sup>36</sup>  $J$ . Finally, the last term in Eq. (2) describes the correction for the double counting (in the absence of orbital polarizations, Eq. (2) should reduce to  $E^{\text{LSDA}}$ ), and is given by<sup>36</sup>

$$E_{dc}[\{n^\sigma\}] = \frac{1}{2}UN(N-1) - \frac{1}{2}J[N^\uparrow(N^\uparrow-1) + N^\downarrow(N^\downarrow-1)], \quad (4)$$

were  $N^\sigma = \text{Tr}(n_{mm'}^\sigma)$  and  $N = N^\uparrow + N^\downarrow$ .

In addition to the usual LDA potential, we find an effective single-particle potential

$$\begin{aligned} V_{mm'}^\sigma &= \sum_{m', m''} \{ \langle m, m'' | V_{ee} | m', m''' \rangle n_{m''m'''}^{-\sigma} \\ &+ (\langle m, m'' | V_{ee} | m', m''' \rangle \\ &- \langle m, m'' | V_{ee} | m''', m' \rangle) n_{m''m'''}^\sigma \} - \\ &- U(N - \frac{1}{2}) + J(N^\sigma - \frac{1}{2}) \end{aligned} \quad (5)$$

to be used in the effective single-particle Hamiltonian

$$\hat{H} = \hat{H}_{\text{LSDA}} + \sum_{mm'} |inlm\sigma\rangle V_{mm'}^\sigma \langle inlm'\sigma|. \quad (6)$$

The Linearized Muffin-Tin Orbitals (LMTO) method in the orthogonal approximation<sup>39</sup> has been used for the LSDA calculations.

Using our Green’s function method we can obtain the effective exchange interaction parameters via the energy variation at small spin rotations<sup>40</sup>. The corresponding expression in the LDA+U scheme takes the form<sup>41</sup>

$$J_{ij} = \sum_{\{m\}} I_{mm'}^i \chi_{mm'm''m'''}^{ij} I_{m''m'''}^j, \quad (7)$$

where the spin-dependent potentials  $I$  are expressed in terms of the potentials of Eq. (5),

$$I_{mm'}^i = V_{mm'}^{i\uparrow} - V_{mm'}^{i\downarrow}, \quad (8)$$

while the effective intersublattice susceptibilities ( $i$  and  $j$ ) are defined in terms of the LDA+U eigenfunctions  $\psi$  as

$$\chi_{mm'm''m'''}^{ij} = \sum_{\mathbf{k}n\mathbf{k}'} \frac{n_{n\mathbf{k}\uparrow} - n_{n'\mathbf{k}\downarrow}}{\epsilon_{n\mathbf{k}\uparrow} - \epsilon_{n'\mathbf{k}\downarrow}} \psi_{n\mathbf{k}\uparrow}^{ilm*} \psi_{n\mathbf{k}\uparrow}^{jlm''} \psi_{n'\mathbf{k}\downarrow}^{ilm'} \psi_{n'\mathbf{k}\downarrow}^{jlm'''}. \quad (9)$$

As a ground state, the standard spin arrangement has been chosen with the spins of Mn1 ions directed down and the spins of Mn2 and Mn3 ions directed up. This arrangement was self-consistent. To check the applicability of the localized spin models to  $\text{Mn}_{12}$  the calculations for the ferromagnetic configurations (all spins up) have also been performed.

## II. ELECTRONIC STRUCTURE AND MAGNETIC MOMENTS

Detailed calculations have been carried out for the three values of  $U = 4, 6$ , and  $8$  eV keeping constant the value of the intra-atomic Hund's exchange parameter  $J = 0.9$  eV, to check the sensitivity of the results with respect to variation in the local Coulomb repulsion  $U$ . For all values of  $U$  used in the calculations, the system turns out insulating with the energy gap between  $1.5 - 2$  eV, and the integer moment of the ferrimagnetic ground state  $\mu_{\text{total}} = 20 \mu_B$ . Dependence of the calculated quantities on the value of  $U$  can be inferred from the data in the Table I, and as one can see, for most of the properties the dependence on  $U$  is reasonably weak. The value  $U = 8$  eV seems to be slightly preferable; it is known that this value gives good agreement with experiments for other manganese-oxide systems, and agrees reasonably well with the independent theoretical calculation<sup>37</sup> giving the value of  $U = 6.9$  eV. Therefore, below we discuss in detail only the case of  $U = 8$  eV.

To begin with, let us compare the results given by LDA and LDA+U approaches. In Figs. 2 and 3, we show the calculated partial densities of states (DOS) for different manganese atoms and for the oxygen atoms belonging to the exchange bridges. Our LDA curves for the DOS are similar to those obtained in Refs. 28,29 using the GGA approach. The main distinction of the LDA+U results as compared with the LDA is the nonzero energy gap instead of the finite DOS at the Fermi level. Moreover, there is a difference in the DOS peaks structure. All manganese ions in  $\text{Mn}_{12}$  molecule are in distorted octahedral coordination, correspondingly, one can see the three peaks of  $t_{2g}$  character situated below the two  $e_g$ -like peaks. For the LDA calculations the spectral density is strongly concentrated within the region  $\pm 2$  eV near the Fermi level, see Fig. 3, while for the LDA+U calculations, the DOS is spread rather uniformly over the region of about 10 eV.

It is known that the LDA+U approach is effective for consideration of charge separation and charge ordering phenomena<sup>36</sup>.  $\text{Mn}_{12}$  molecules also exhibit  $\text{Mn}^{3+} - \text{Mn}^{4+}$  disproportionality, which has been directly demonstrated by the measurements of the X-ray absorption spectra<sup>43</sup>. The majority spin DOS curves (see Fig. 2) demonstrate three occupied  $t_{2g}$  peaks and two empty  $e_g$  peaks for Mn1, while for Mn2 and Mn3 ions only one  $e_g$  peak is empty; this picture indeed corresponds to the charge disproportionality detected in the experiments.

Several remarks are in order. There are indications that the manganese-oxygen bonds are considerably covalent, and  $3d$  states of manganese are highly hybridized with  $2p$  states of oxygen. As can be seen in Fig. 2, the main features in the partial DOS of manganese ions have counterparts in the partial DOS of oxygen ions. Another indication of the strong covalence is the discrepancy between the sum of the local  $3d$ -moments of Mn ions and the total magnetic moment of the molecule which is cal-

culated from the total DOS. The difference, which is of order of  $2\mu_B$ , can be attributed to the partial moments of oxygens estimated to be of order of  $0.05\mu_B$ .

The value of the energy gap calculated within LDA+U scheme varies from 1.78 eV to 2.01 eV with the change in the value of  $U$  from 6 eV to 8 eV. Recent optical measurements<sup>25</sup> show the features in the absorption and reflection spectra in the region of the charge-transfer excitations at 1.7 eV, 2.0 eV, and 2.4 eV. Magneto-optical measurements<sup>45</sup> also show the latter feature. These values are in very good agreement with the calculated energy gap.

## III. INTRAMOLECULAR EXCHANGE INTERACTIONS

At present, there is no reliable quantitative information about the intramolecular exchange couplings in the  $\text{Mn}_{12}$  molecules, making difficult the validation of the corresponding computational results. Crude estimates for the exchange couplings, based on the comparison with different manganese-oxygen compounds, have been presented in Ref. 44. Quantitative evaluation of the exchange constants has been performed in Ref. 24 using the results of the megagauss-field experiments, however the magnetization curves appeared to be not very sensitive to the values of the exchange parameters. Another quantitative approach, based on the inelastic neutron scattering data, has been undertaken<sup>26</sup>, but a simplified eight-spin model was used which makes the fitting not conclusive (see the discussion of various possible sets of parameters in Ref. 26). Therefore, we believe that it makes sense to focus the discussion of our results on qualitative trends in the calculated parameters instead of their exact values.

The exchange parameters have been calculated for different values of  $U$ , see Table I. As expected for the superexchange mechanism, the values of the couplings decrease with increasing  $U$ ; again, below we discuss only the values corresponding to  $U = 8$  eV. We have compared the calculated values of the exchange parameters with the data suggested in Refs. 24,44, see the Table III. In this Table, we have shown only the interactions between relatively closely situated manganese ions; the exchange parameters between distant ions do not exceed 2–3 K. As one can see, the values obtained in our calculations are closer to those resulting from the analysis of the megagauss-field experiments, while the data suggested from general chemical consideration are bigger by about a factor of three. However, the more interesting fact is that the exchanges between the  $\text{Mn}^{4+}$  ions are not all equal, as assumed in Refs. 24,44. The  $\text{Mn}^{4+}$  ions in  $\text{Mn}_{12}$  molecules are arranged in the four corners of a cubane (distorted cube, see Fig. 4) while the other four corners are occupied by the oxygens providing superexchange bridges between the manganese ions. Therefore, the manganesees form a distorted tetrahedron with four short edges of the length 5.33 a.u. and two long edges of

the length of 5.56 a.u., and the angles Mn-O-Mn in the cubane which correspond to the long and short edges of the manganese tetrahedron are  $95.5^\circ$  and  $100.6^\circ$ . In spite of the moderate difference in the angles and lengths of the exchange pathways, the calculated coupling parameters turn out very different; the interactions  $J'_3$  for the longer pathways are about three times smaller than the interactions  $J_3$  for the shorter ones.

All the previous considerations<sup>24,26,44</sup> of the exchange interactions in  $Mn_{12}$  were based on the localized Heisenberg model, assuming that the values of the magnetic moments and the exchange parameters do not depend on the spin arrangement of the molecule. To check the accuracy of this assumption, we have performed the calculations for the totally ferromagnetic spin configuration, when all manganese spins are directed up, using the parameters  $U = 8$  eV and  $J = 0.9$  eV. The results are the following:

$$\begin{aligned}\mu_{Mn1} &= 3.06 \mu_B, \mu_{Mn2} = 3.55 \mu_B, \mu_{Mn3} = 3.85 \mu_B, \\ \text{gap} &= 1.63 \text{ eV}, \\ J_1 &= -36 \text{ K}, J_2 = -18 \text{ K}, \\ J_3 &= -22 \text{ K}, J'_3 = +1 \text{ K}, J_4 = -6 \text{ K}.\end{aligned}$$

Comparing these results with the Tables II, III, we see that the values of the moments vary by no more than 5%, but the exchange integrals  $J_1$  and  $J_3$  decrease by about 25-30%, and the exchange  $J'_3$  almost vanishes. These changes are due to the strong covalency effects and the corresponding partial delocalization of the 3d-electrons discussed above.

The energy of the exchange excitations in the  $Mn_{12}$  molecule, e.g., the difference between the ground-state  $S = 10$  multiplet and the close excited multiplet, can be crudely obtained from a simple mean-field estimate, assuming that the pairs  $Mn^{4+}$ - $Mn^{3+}$  ions form stiff dimers with the total spin  $1/2$  (i.e.,  $J_1 \rightarrow -\infty$ ). Then, the energy of the ground state is  $E_0 = -2J_3 - J'_3 - 32J_4 + 16J_2$  and the energy of the first excited state is  $E_1 = 2J_3 + J'_3$ , so that the excitation energy is 52 K. This number is close to the values 58-66 K obtained in the neutron scattering experiments<sup>23</sup>. Of course, this agreement should not be taken literally (it is a semiclassical estimate, the value of  $J_1$  is not big enough, we did not take into account the contributions of relativistic interactions which could be comparable to the exchange contribution<sup>26</sup>, etc.), but we believe that this indicates qualitative adequacy of the calculated exchanges.

#### IV. CONCLUSIONS

We have applied the LDA+U approach to the study of intramolecular magnetic interactions in  $Mn_{12}$ -acetate system. We have shown that the account of the on-site Coulomb interactions provides a good description of the main features of the electronic and magnetic structure, giving the finite energy gap and the integer value for the magnetic moment of the molecule. The calculated partial magnetic moments, charge disproportionality between the Mn1 and Mn2, Mn3 ions, and the energy gap are in agreement with existing experimental data. The calculations show significant  $p$ - $d$  hybridization and considerable covalency effects, and the contribution of delocalized electrons in the total magnetic moment of the molecule is about 10%. The calculated intramolecular exchange interactions are in qualitative agreement with the existing data. An interesting result of the calculations is that the interactions between the  $Mn^{4+}$  ions situated in the inner cubane are not all equal, differing by about a factor of three for different exchange-coupled pairs. The applicability of localized Heisenberg model has been estimated by comparing the values of the exchange interactions for different spin configurations (ground-state ferrimagnetic and totally ferromagnetic), and corresponding variation of the coupling parameters is about 30%.

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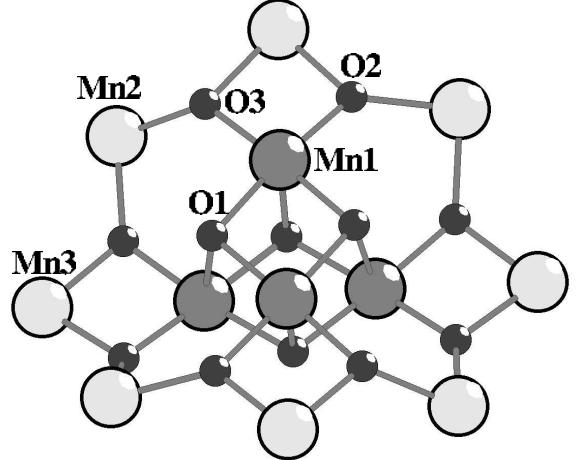


FIG. 1: The sketch of the arrangement of the manganese and oxygen ions in the  $Mn_{12}$  molecule. Big dark-grey circles represent the  $Mn^{4+}$  ions, big light-grey circles —  $Mn^{3+}$  ions, and small dark circles are the bridging oxygens. Non-equivalent manganese ions  $Mn1$ ,  $Mn2$ ,  $Mn3$ , and the oxygens  $O1$ ,  $O2$ ,  $O3$  bridging them are indicated.

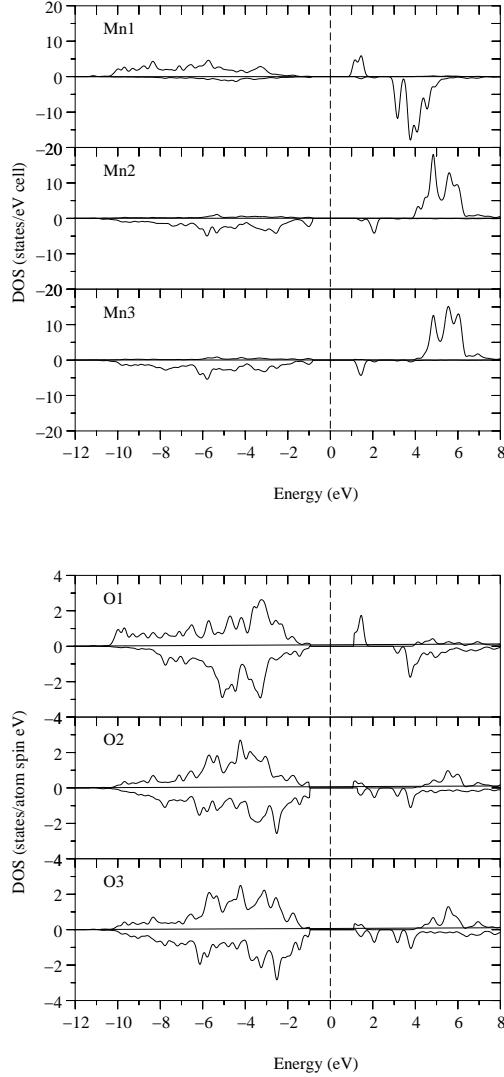


FIG. 2: Partial densities of states for different manganese ( $d$  orbitals) and oxygen ( $p$  orbitals) atoms within the LDA+U approach. The values  $U = 8$  eV and  $J = 0.9$  eV have been used.

TABLE I: The calculated magnetic moments (in  $\mu_B$ ) of the manganese ions, values of the exchange interaction parameters (in K) and the energy gap (in eV) for different values of  $U$  (in eV). The value of  $J$  is 0.9 eV. The parameters of the exchange interactions  $J_3$  correspond to the exchange between the closest Mn1 ions in the cubane (see text).

$U$	$\mu_{\text{total}}$	$\mu_{\text{Mn1}}$	$\mu_{\text{Mn2}}$	$\mu_{\text{Mn3}}$	$J_1$	$J_2$	$J_3$	$J_4$	gap
4.0	20	-2.72	3.44	3.65	-53	-47	-37	-19	1.35
6.0	20	-2.80	3.55	3.76	-49	-37	-33	-12	1.78
8.0	20	-2.92	3.52	3.84	-47	-26	-30	-7	2.01

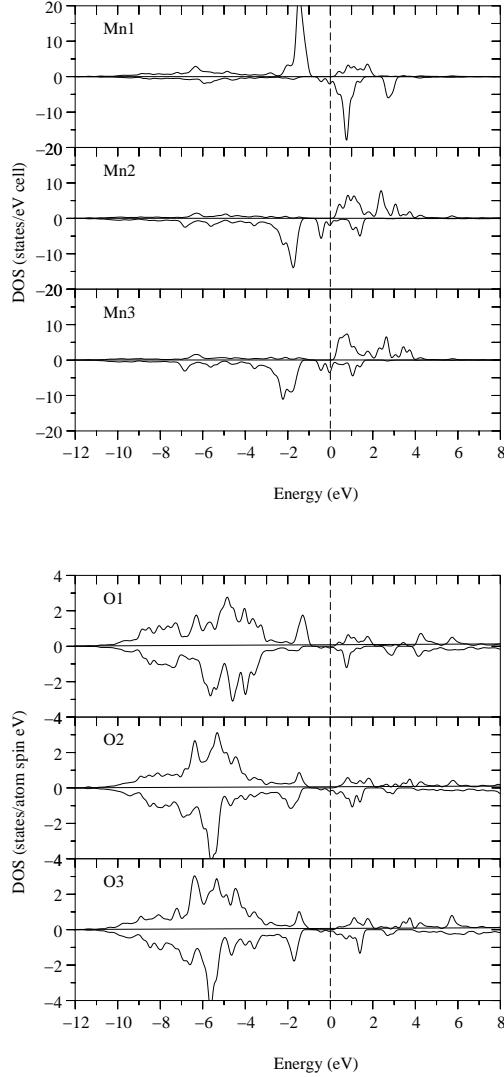


FIG. 3: Partial densities of states for different manganese ( $d$  orbitals) and oxygen ( $p$  orbitals) atoms calculated within the LDA approach.

TABLE II: The comparison of the calculated magnetic moments (in  $\mu_B$ ) with the existing theoretical and experimental data. **1** are the data calculated by Pederson et al., Ref. [26,27]; **2** — the data calculated by Zeng et al., Ref. [28] (only the contribution of  $d$ -states is presented); **Exp** — the experimental results of Robinson et al., Ref. [41]. The next two columns are the results of our calculations done within the LDA and LDA+U methods. LDA+U results for the values  $U = 8$  eV,  $J = 0.9$  eV are shown.

	<b>1</b>	<b>2</b>	<b>Exp</b>	LDA	LDA+U
$\mu_{\text{Mn}1}$	-2.6	-3.05	-2.34	-2.41	-2.92
$\mu_{\text{Mn}2}$	3.6	3.89	3.69	3.53	3.52
$\mu_{\text{Mn}3}$	3.6	4.04	3.79	3.55	3.84
$\mu_{\text{total}}$			20.56	19.00	20.00

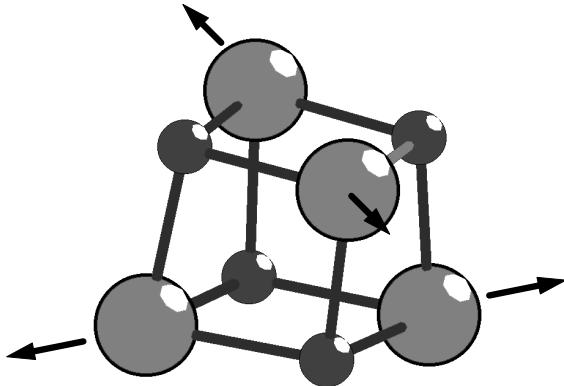


FIG. 4: The sketch of the arrangement of the manganese and oxygen ions in the inner cubane of  $Mn_{12}$  molecule. Arrows show the directions of the displacement of the Mn ions which lead to the formation of the inner cubane instead of the perfect cube.

TABLE III: The comparison of the calculated values of the exchange parameters (last line of the table) with the existing data. **3** — the data suggested by Sessoli et al., Ref. [43]; **4** — the data of Platonov et al., Ref. [23]. LDA+U results for the values  $U = 8$  eV,  $J = 0.9$  eV are shown. The parameters of the exchange interactions  $J_3$  and  $J'_3$  correspond to the exchange inside different pairs of Mn1 ions in the cubane (see text). All values are given in Kelvin.

	$J_1$	$J_2$	$J_3$	$J'_3$	$J_4$
<b>3</b>	-215	-86	-86	—	(?)30
<b>4</b>	-86	-20	-23	—	0.0
LDA+U	-47	-26	-30	-10	-7